



Endo and Exo Coordination to Cofacial Binuclear Copper(II) Complexes

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(Received: 6 July 1999; in final form: 14 March 2000)

Key words: bis(β -diketone), cofacial, binuclear, copper(II), complexes, host, guest

Abstract

A structural study of internal (*endo*) and external (*exo*) coordination to cofacial binuclear complexes is reported. $\text{Cu}_2(\text{NBA})_2(\text{NBAH}_2=3,3'-[2,7\text{-naphthalenediylbis(methylene)]-bis(2,4\text{-pentanedione})])$ is large enough to accommodate 2-methylpyrazine as an intramolecularly coordinated guest molecule. $\text{Cu}_2(\text{NBA})_2(\mu\text{-}(2\text{-Mepyz}))\cdot 4\text{CH}_2\text{Cl}_2$, $\text{Cu}_2\text{C}_{53}\text{H}_{58}\text{N}_2\text{O}_8\text{Cl}_8$, orthorhombic, space group *Pnma* (No. 62); $a = 22.4674(11)$; $b = 22.230(2)$; $c = 11.4520(6)$ Å; $V = 5719.6(6)$ Å³ (at 100 K); $Z = 4$; $R = 0.058$; $R_w = 0.167$ for 344 parameters and 5339 reflections with $I > 2\sigma(I)$. The $\text{Cu}_2(\text{NBA})_2(\mu\text{-}(2\text{-Mepyz}))$ molecules possess crystallographic *m* symmetry, with the $\text{Cu}\cdots\text{Cu}$ vector ($\text{Cu}\cdots\text{Cu}'$ 7.4801(8) Å) perpendicular to the mirror plane; this requires disorder in the 2-Mepyz guests. The two “Cu(acac)₂” moieties (acacH = 2,4-pentanedione) are not quite parallel (dihedral angle between (acac)₂ planes = 3.93(7)°), forming a slightly wider opening on the side of the methyl group in the 2-Mepyz guest. On the other hand, the cavity in $\text{Cu}_2(\text{XBA})_2$ ($\text{XBAH}_2 = 3,3'-[1,3\text{-phenylenebis(methylene)]-bis(2,4\text{-pentanedione})])$ is smaller, so that CH_3CN must bind externally. $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$, $\text{Cu}_2\text{C}_{43}\text{H}_{52.5}\text{N}_{3.5}\text{O}_9$, monoclinic, space group *P2₁/c* (No. 14); $a = 11.7361(16)$; $b = 14.197(3)$; $c = 13.299(3)$ Å; $\beta = 92.22(2)^\circ$; $V = 2214.3(7)$ Å³ (at 100 K); $Z = 2$; $R = 0.044$; $R_w = 0.124$ for 275 parameters and 4983 reflections with $I > 2\sigma(I)$. This structure contains centrosymmetric $\text{Cu}_2(\text{XBA})_2$ units ($\text{Cu}\cdots\text{Cu}'$ 4.8302(12) Å) with externally coordinated CH_3CN ligands. The crystal packing in $\text{Cu}_2(\text{NBA})_2(\mu\text{-}(2\text{-Mepyz}))\cdot 4\text{CH}_2\text{Cl}_2$, which contains close π contacts between layers of $\text{Cu}_2(\text{NBA})_2(\mu\text{-}(2\text{-Mepyz}))$ moieties, is also similar to that in three other crystalline host–guest adducts $\text{M}_2(\text{NBA})_2(\mu\text{-G})$. $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{-CN}\cdot\text{H}_2\text{O}$ does not contain similar layers of molecules, presumably because the adduct molecules do not have the same type of exposed flat surfaces.

Supplementary data relating to this article (two files in CIF format) have been deposited with the Cambridge Structural Database.

Introduction

Numerous macrocyclic polynuclear metal complexes have been prepared in which the metal atoms will bind small guest molecules [1]. Some of these are based on multidentate macrocyclic ligands that coordinate two metal atoms, which then bind guests such as imidazole, dicarboxylate anions, or O₂ (see structure **I**) [2]. Other hosts contain two or more porphyrin moieties: these include diporphyrins with rigid or flexible bridging groups (structure **II**) [3], and an elegant series of cyclic molecules with two, three, four, or six metalloporphyrin units that are able to bind guest molecules very tightly (see example as structure **III**) [4].

In our work, we have used cofacial bis(β -diketone) complexes such as $\text{Cu}_2(\text{XBA})_2$ and $\text{Cu}_2(\text{NBA})_2$ (see Chart 2) as “metalloreceptor” [5] host molecules. We proposed that both “empty” complexes (represented as structure **IV** below)

can bind pyridine in the outer axial positions represented by L (*exo*; structure **V**) [6, 7], but that $\text{Cu}_2(\text{NBA})_2$ is large enough to accommodate bidentate Lewis bases (G) such as Dabco (1,4-diaza-bicyclo[2.2.2]octane) [7] and 2,5-dimethylpyrazine [8] in an intramolecular fashion (*endo*; structure **VI**). We now report a study of these modes of binding in two X-ray analyses, a detailed comparison of the *endo* binding of 2-methylpyrazine to our previous results with other guests, and similarities in crystal packing among several of the $\text{M}_2(\text{NBA})_2$ host–guest complexes.

Experimental

Materials and procedures

$\text{Cu}_2(\text{XBA})_2$ [6, 9] and $\text{Cu}_2(\text{NBA})_2\cdot 2\text{CHCl}_3$ [8] were prepared by published procedures. 2-Methylpyrazine (2-Mepyz) was obtained from the Aldrich Chemical Co. and

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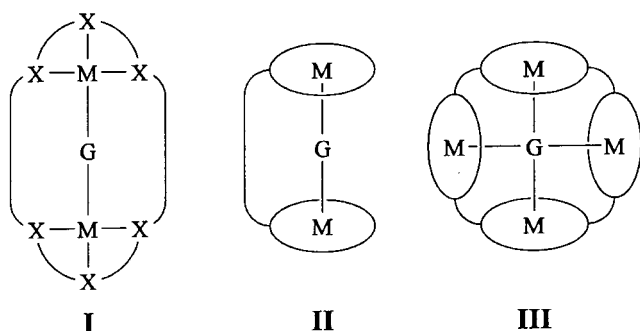


Chart 1. Schematic structures of several metalloreceptors. X = donor atom; G = guest molecule.

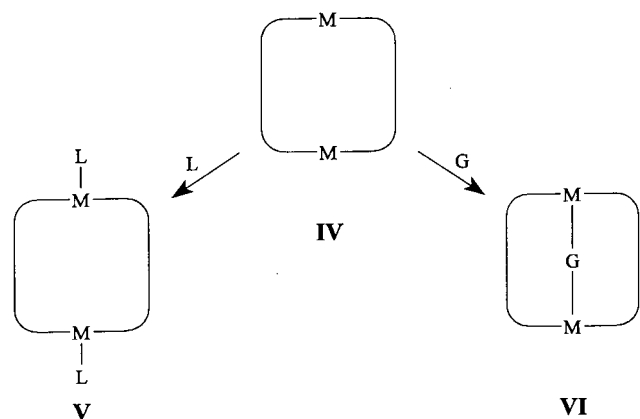
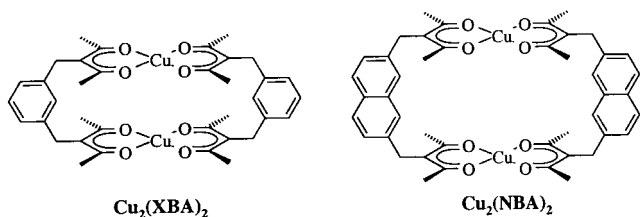


Chart 2. Top: Structure drawings for cofacial bis(β -diketone) complex hosts. Bottom: (IV-VI): Internal (*endo*) and external (*exo*) coordination modes for $\text{Cu}_2(\text{XBA})_2$ and $\text{Cu}_2(\text{NBA})_2$.

used without further purification. Other materials were reagent or spectrophotometric grade and were used as received.

Preparation of $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-mepyz)})\cdot 4\text{CH}_2\text{Cl}_2$

Solutions prepared from $\text{Cu}_2(\text{NBA})_2\cdot 2\text{CHCl}_3$, which are initially olive-green in color, turn turquoise on treatment with 2-methylpyrazine. The turquoise adduct was crystallized by layering a CH_2Cl_2 solution prepared from $\text{Cu}_2(\text{NBA})_2\cdot 2\text{CHCl}_3$ first with benzene- CH_2Cl_2 (ca. 1:1 v/v, to retard mixing with the 2-Mepyz) and then with pure liquid 2-Mepyz. After 24–48 h, deep turquoise parallelepipeds had formed.

Preparation of $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot \text{H}_2\text{O}$

This compound was prepared by layering a chloroform solution of $\text{Cu}_2(\text{XBA})_2$ with acetonitrile. Crystals formed over a period of several days. The majority of the product con-

sisted of small olive-green needles of $\text{Cu}_2(\text{XBA})_2$, but a few block-shaped turquoise crystals of the desired CH_3CN adduct usually formed as well. A greater fraction of the crystalline CH_3CN adduct was formed after a longer period of exposure to laboratory air, possibly reflecting the importance of water in the crystallization.

Both $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})\cdot 4\text{CH}_2\text{Cl}_2$ and $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot \text{H}_2\text{O}$ become opaque rapidly when exposed to the atmosphere, probably due to loss of solvent. In the case of $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot \text{H}_2\text{O}$, the residue is an olive-green powder whose spectroscopic properties are identical to those of freshly prepared $\text{Cu}_2(\text{XBA})_2$. Satisfactory microanalytical data could not be obtained for the complexes because of this solvent loss. For X-ray analyses, crystals were mounted on glass fibers and immediately placed in the cold $\text{N}_2(\text{g})$ stream on the diffractometer, which prevented solvent loss. The densities of the crystals were measured by flotation, using a mixture of CCl_4 and the mother liquor from crystallization.

X-ray analyses: general remarks

Diffraction data for both crystals were collected at 100 K on an Enraf-Nonius CAD4 diffractometer fitted with an Oxford Cryostream, a graphite monochromator and a $\text{MoK}\alpha$ source, using the $\theta - 2\theta$ scan method. Final unit cell constants were determined from the orientations of 25 centered high-angle reflections. The intensities were corrected for absorption using ψ scan data for five reflections. Additional crystallographic data, and further data collection and refinement parameters, are summarized in Table I. Selected bond lengths and angles are presented in Tables 2 and 3. Drawings for the two structures are in Figures 1 and 2.

X-ray analysis of $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})\cdot 4\text{CH}_2\text{Cl}_2$

Choice of space group

Diffraction data were originally collected at room temperature for a monoclinic unit cell ($a = 11.572(3)$, $b = 22.786(5)$, $c = 22.382(6)$ Å, $\beta = 90.06(2)^\circ$, $\text{CuK}\alpha$ source) and the structure solved in $P2_1/n$. In this space group, the asymmetric unit contains one complete $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})$ unit. Early in this refinement, there were several indications that $P2_1/n$ was incorrect: the $\text{Cu}\cdots\text{Cu}$ vector lay nearly exactly along c , the U values for the two Cu atoms were strongly correlated, and two equally likely positions appeared for the methyl group in the Mepyz guest. These observations suggested that a mirror plane perpendicular to c , bisecting the $\text{Cu}\cdots\text{Cu}$ vector, had been overlooked. No higher-symmetry monoclinic space groups are available; however, if b were exactly 90° , the symmetry of $P2_1/n$, along with the mirror plane perpendicular to c , would give $Pbnm$, an alternate setting of the space group $Pnma$. Refinement was carried out in the orthorhombic space group, but the number of observed reflections was low (2453 with $I > 1\sigma(I)$) and the required disorder of the guest and solvent was difficult to model. We therefore measured diffraction data for a second crystal at 100 K with a $\text{MoK}\alpha$ source.

Table 1. Data collection and refinement parameters^a

	Cu ₂ (NBA) ₂ (μ-(2-Mepyz))-4CH ₂ Cl ₂	Cu ₂ (XBA) ₂ (CH ₃ CN) ₂ ·1.5CH ₃ CN·H ₂ O
Formula	Cu ₂ C ₅₃ H ₅₈ N ₂ O ₈ Cl ₈	Cu ₂ C ₄₃ H _{52.5} N _{3.5} O ₉
fw	1261.77	889.50
Color	turquoise	turquoise
Habit	parallelepiped	prism
<i>a</i> /Å	22.4674(11)	11.7361(16)
<i>b</i> /Å	22.230(2)	14.197(3)
<i>c</i> /Å	11.4520(6)	13.299(3)
β /°	90	92.22(2)
<i>V</i> /Å ³	5719.6(6)	2214.3(7)
<i>Z</i>	4	2
Space group	<i>Pnma</i> , No. 62	<i>P2₁/c</i> , No. 14
Temp/K	100 ± 1	100 ± 1
ρ_m (300 K), ρ_x /g cm ⁻³	1.42(2), 1.465	1.30(2), 1.334
λ /Å	0.71073 (Mo K α)	0.71073 (MoK α)
μ /cm ⁻¹	11.7	10.2
Cryst dimen/mm	0.20 × 0.38 × 0.45	0.25 × 0.38 × 0.40
Transm coeff	0.66–0.79	0.64–0.80
θ range/°	2–30	2–30
(<i>h k l</i>) collected	(–31 –31 0) → (0 21 14)	(–16 0 –18) → (16 19 12)
Unique refls measd	8083	6452
Refls obsd (<i>I</i> > 2 σ (<i>I</i>))	5339	4983
<i>R</i> _{int}	0.027	0.026
Parameters	344	275
Decay, std rf	2.0%	1.0%
<i>R</i> (<i>F</i>) ^b (obsd data)	0.058	0.044
<i>R</i> (<i>F</i>) ^b (all data)	0.106	0.065
<i>R_w</i> (<i>F</i> ²) ^c (obsd data)	0.167 ^d	0.124 ^e
<i>R_w</i> (<i>F</i> ²) ^c (all data)	0.204 ^d	0.142 ^e
GOF ^f	0.978	0.833
Max shift/esd	–0.51	0.001
Max resid	1.24 e Å ⁻³	1.25 e Å ⁻³
Min resid	–1.10 e Å ⁻³	–0.54 e Å ⁻³

^a In Tables 1–5, estimated standard deviations in the least significant digits of the values are given in parentheses.

^b $R(F) = \sum \|F_o\| - |F_c| / \sum |F_o|$.

^c $R_w(F^2) = \sqrt{(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)}$.

^d $w = 1/(\sigma^2(F_o^2) + (0.1302P)^2 + 2.8665P)$; $P = (F_o^2 + 2F_c^2)/3$.

^e $w = 1/(\sigma^2(F_o^2) + (0.0963P)^2 + 3.9500P)$; $P = (F_o^2 + 2F_c^2)/3$.

^f $GOF = \sqrt{(\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param}))}$.

Table 2. Selected interatomic distances/Å^a

A. Cu ₂ (NBA) ₂ (μ-(2-Mepyz))-4CH ₂ Cl ₂					
Cu···Cu'	7.4801(8)	N1P-C6P	1.34	C5···C5'	7.671(8)
Cu-O1	1.918(2)	N2P-C4P	1.34	C7···C7'	7.396(8)
Cu-O2	1.925(3)	N2P-C5P	1.35	C11···C11'	7.676(8)
Cu-O3	1.919(3)	C3P-C4P	1.38	O1···O1'	8.010(5)
Cu-O4	1.923(3)	C5P-C6P	1.36	O2···O2'	7.666(5)
Cu-N1P	2.376(11)	C6P-C8P	1.53	O3···O3'	7.564(5)
Cu-N2P'	2.341(11)	C1···C1'	7.869(8)	O4···O4'	7.811(5)
N1P-C3P	1.35				
B. Cu ₂ (XBA) ₂ (CH ₃ CN) ₂ ·1.5CH ₃ CN·H ₂ O					
Cu···Cu'	4.8302(12)	Cu-O4	1.9083(17)	C19-C20	1.450(4)
Cu-O1	1.9260(17)	Cu-N1	2.368(2)	O1···O3'	4.503(3)
Cu-O2	1.9246(17)	N1-C19	1.138(4)	O2···O4'	4.547(2)
Cu-O3	1.9210(18)				

^a In Tables 2 and 3, primes represent mirror- and inversion-related atoms in the structures of Cu₂(NBA)₂(μ-(2-Mepyz))-4CH₂Cl₂ and Cu₂(XBA)₂(CH₃CN)₂·1.5CH₃CN·H₂O, respectively. In Cu₂(NBA)₂(μ-(2-Mepyz))-4CH₂Cl₂, some distances and angles involving the 2-Mepyz guest are given without esd values, since the guest was treated as a rigid body in the final refinement.

Table 3. Selected bond angles^o

A. Cu ₂ (NBA) ₂ (μ-(2-Mepyz))-4CH ₂ Cl ₂					
O1-Cu-O2	91.94(10)	O4-Cu-N1P	94.6(2)	Cu'-N2P-C5P	124.7(4)
O1-Cu-O3	170.78(11)	O1-Cu-N2P'	94.3(2)	C4P-N2P-C5P	117.4
O1-Cu-O4	88.22(10)	O2-Cu-N2P'	94.7(2)	N1P-C3P-C4P	121.1
O2-Cu-O3	86.89(11)	O3-Cu-N2P'	94.9(2)	N2P-C4P-C3P	121.7
O2-Cu-O4	172.20(11)	O4-Cu-N2P'	93.1(2)	N2P-C5P-C6P	120.2
O3-Cu-O4	91.70(11)	Cu-N1P-C3P	117.1(4)	N1P-C6P-C5P	123.6
O1-Cu-N1P	92.0(2)	Cu-N1P-C6P	126.6(4)	N1P-C6P-C8P	125.0
O2-Cu-N1P	93.2(2)	C3P-N1P-C6P	115.9	C5P-C6P-C8P	111.3
O3-Cu-N1P	97.2(2)	Cu'-N2P-C4P	117.9(4)		
B. Cu ₂ (XBA) ₂ (CH ₃ CN) ₂ ·1.5CH ₃ CN·H ₂ O					
O1-Cu-O2	90.81(7)	O2-Cu-O3	89.41(7)	O3-Cu-N	94.61(9)
O1-Cu-O3	170.13(8)	O2-Cu-O4	171.46(7)	O4-Cu-N	99.69(8)
O1-Cu-O4	87.02(7)	O2-Cu-N	88.72(8)	Cu-N-C19	174.2(2)
O1-Cu-N	95.26(9)	O3-Cu-O4	91.32(7)	N-C19-C20	179.3(3)

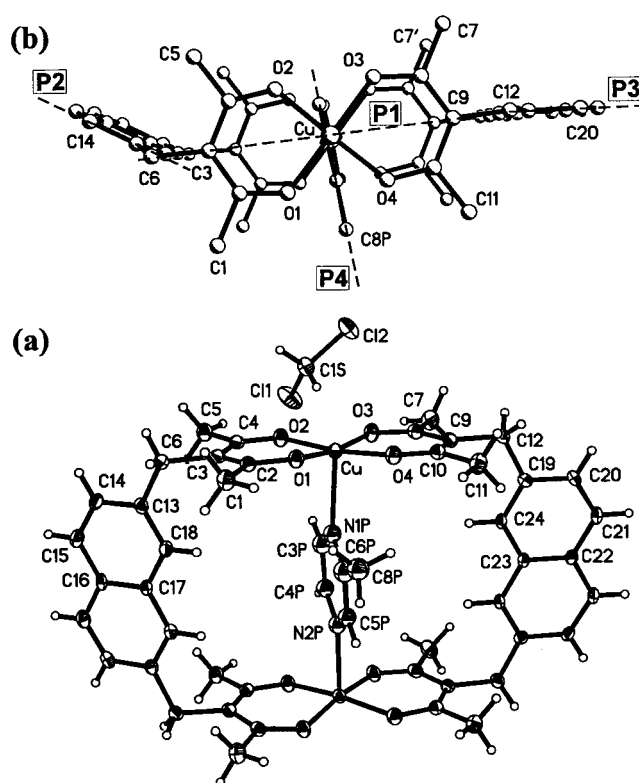


Figure 1. SHELXTL [11] drawings for Cu₂(NBA)₂(μ-(2-Mepyz))-4CH₂Cl₂. (a) Side view, with ellipsoids at the 50% probability level. The solvent molecule related by the mirror plane, and the two disordered solvent molecules, are omitted. (b) Top view, in ball-and-stick representation, showing orientation of least-squares planes (indicated by dashed lines and labeled P1, P2, P3 and P4); H atoms and solvent molecules are omitted for clarity. Primed and unprimed atoms are related by the mirror plane at $y = 1/4$.

The diffraction intensities at 100 K were stronger and the choice of the orthorhombic unit cell less ambiguous. The structure was readily solved by direct methods (SHELXS86 [10]) in *Pnma* and also in the noncentrosymmetric space group *Pn2₁a*.

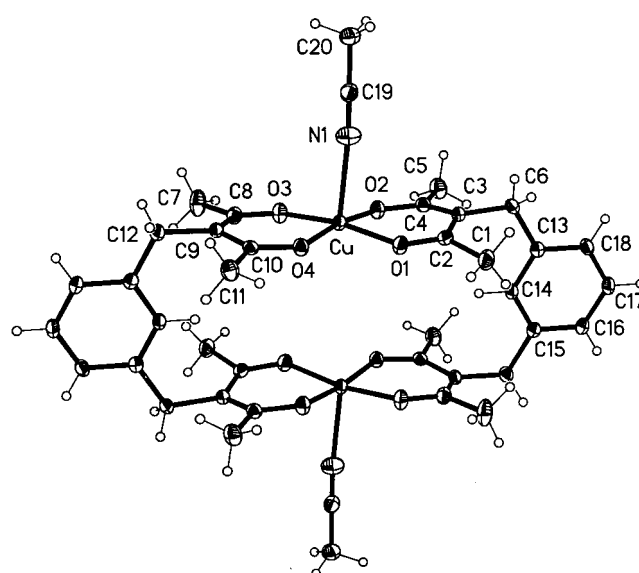


Figure 2. SHELXTL [11] drawing for Cu₂(XBA)₂(CH₃CN)₂·1.5CH₃CN·H₂O, with ellipsoids at the 50% probability level. Solvent molecules are not shown.

Refinement in *Pn2₁a*

The space group *Pn2₁a*, an alternate setting of *Pna2₁*, is compatible with the observed systematic absences, though it does not include the mirror plane perpendicular to Cu...Cu suggested by room temperature refinement. In this space group, the full molecule is the asymmetric unit, and the structure is noncentrosymmetric. Refinement in *Pn2₁a* led to chemically unreasonable interatomic distances. In addition, the 2-Mepyz guest refined reasonably but the 'shadow' methyl group related by the mirror appeared in difference maps, and the solvent molecules near the mirror plane were also disordered in *Pn2₁a*. Therefore, we concluded that the most appropriate space group is the centrosymmetric one, and the mirror plane is present for the overwhelming majority of the scattering matter.

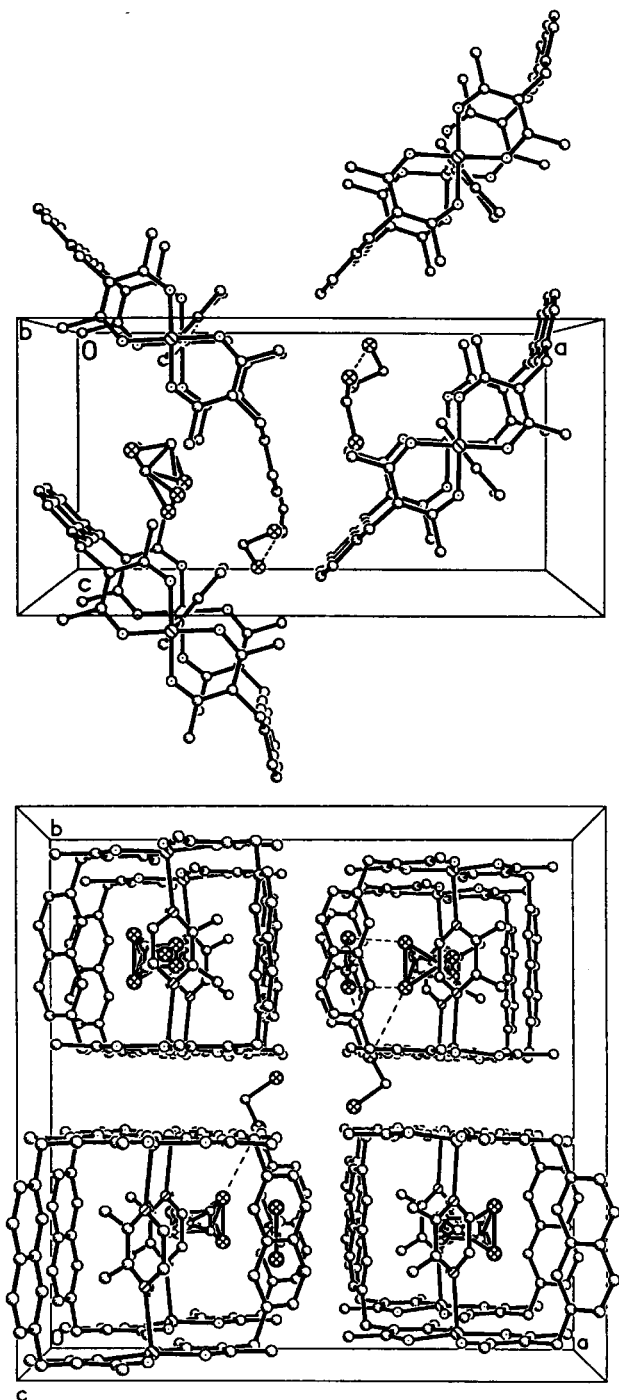


Figure 3. Packing diagrams for $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})\cdot 4\text{CH}_2\text{Cl}_2$. (Top) view along b , showing "herringbone" packing of adjacent molecules, along with disordered solvent region between molecules. (Bottom) view along c , showing the alignment of molecules in layers perpendicular to b .

Refinement in $Pnma$

All nonhydrogen atoms but one in the host, all nonhydrogen atoms in the guest except the disordered methyl carbon, and most of the CH_2Cl_2 atoms appeared in the E -map (SHELXS86 [10]). The first difference map revealed the remaining nonhydrogen atoms. The guest was modeled with a single complete 2-Mepyz molecule of occupancy 0.50, which was treated as a rigid group, and whose geometry was taken from the $Pna2_1$ refinement. SHELXL-97 [11] was

used for the final cycles of refinement, which was carried out as follows. U_{iso} values for the guest were restrained to be similar, and U_{iso} for N1P was constrained to be equal to U_{iso} for N2P. H atoms were treated in two ways. The β -diketone methyl H atoms were restrained to ideal geometry, with $U_{\text{iso}} = 1.5 \times U_{\text{eq}}(\text{C})$, and methyl groups were refined by rotating about the C–C bond to best fit the electron density. All other H atoms were treated as riding at fixed distances with $U_{\text{iso}} = 1.2 \times U_{\text{eq}}(\text{C})$. For the β -diketone methyl H atoms, the observed peaks indicated the same eclipsed O–C–C–H conformation observed in several of our bis(β -diketone) and related structures [6–8, 12]. After the final rigid-group refinement, the orientation of the guest methyl group, originally optimized by rotation as for the host methyl groups, was checked to make sure that it still fit the observed electron density well in that region.

There are four CH_2Cl_2 molecules per $\text{Cu}_2(\text{NBA})_2$ unit in the structure, as follows: C11–C1S–Cl2, ordered and in a general position (total 2 molecules per $\text{Cu}_2(\text{NBA})_2$ unit), was refined anisotropically. The other two CH_2Cl_2 molecules are disordered about the mirror plane. One (C13–C2S–Cl4, 1.0 per $\text{Cu}_2(\text{NBA})_2$ unit) was modeled with restrained distances and angles. The fourth solvent molecule is more severely disordered (C15–C3S–Cl6/Cl7 with C15–C4S–Cl8, total 1.0 per $\text{Cu}_2(\text{NBA})_2$ unit) and was also refined with restraints. All of the four highest peaks in the final difference Fourier map ($1.08\text{--}1.24 \text{ e } \text{\AA}^{-3}$) were near C or Cl atoms in a disordered solvent region (C15–C3S–Cl6/Cl7 and C15–C4S–Cl8).

X-ray analysis of $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot \text{H}_2\text{O}$

The space group for this compound was determined uniquely by the systematic absences. The structure was solved by direct methods using the MolEN set of programs [13], and then refined using SHELXL-97 [11]. All nonhydrogen atoms were refined anisotropically, except for two of the partially occupied solvent atoms (C1S and O6), which were refined isotropically. Hydrogen atoms were placed in calculated positions, with fixed $U_{\text{iso}} = 1.2 \times U_{\text{eq}}(\text{C})$, except for those in methyl groups, for which $U_{\text{iso}} = 1.5 \times U_{\text{eq}}(\text{C})$. The orientation of each methyl group was optimized by refining a rotational parameter. H atoms for the partially populated solvent molecules were not included in the model.

Results and discussion

Structure of $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})\cdot 4\text{CH}_2\text{Cl}_2$

This structure contains $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2-Mepyz)})$ molecules (see Figure 1) with crystallographically imposed mirror symmetry. The molecules are arranged in layers perpendicular to b , about the common mirror plane, with $\text{Cu}\cdots\text{Cu}'$ vectors ($7.4801(8) \text{ \AA}$) along b . The naphthalene C atoms C16, C17, C22 and C23 lie in the mirror plane, and the 2-Mepyz guest molecule is disordered across it. (We have modeled the guest here as a complete 2-Mepyz molecule, of occupancy 1/2, together with its mirror image.) The metal

atoms are in square-pyramidal environments, with Cu displaced toward the apical N atoms by 0.142(1) Å out of the least-squares plane of the four O atoms.

In the other pyrazine-based adduct we have studied previously, $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2,5-Me}_2\text{pyz)})\cdot 4\text{CH}_2\text{Cl}_2$ [8], the molecules lie on sites of $2/m$ (C_{2h}) symmetry, which requires the guest molecules to be disordered (i.e. each of the four C atoms in the pyrazine ring is equally likely to have a CH_3 group attached). As a result, the $(\text{acac})_2$ least-squares planes on opposing Cu atoms are parallel, and the average N atom positions lie on the $\text{Cu}\cdots\text{Cu}$ vector. In the present structure, on the other hand, the crystallographic symmetry is only m (C_s). Mirror symmetry can be achieved by a simple two-fold disorder of the 2-Mepyz, as observed here: the methyl groups are on only one side of the 2-Mepyz guest. This lower-symmetry disorder model has two effects: First, the mirror-related $(\text{acac})_2$ moieties are tilted away from parallelism due to the steric effects of the guest; normals to the least-squares planes through these two $(\text{acac})_2$ moieties make an angle of $3.93(7)^\circ$. The lack of parallelism of the two $(\text{acac})_2$ planes can be thought of as a rotation of these planes (in opposite directions, as required by the mirror symmetry of the molecule) about an axis passing approximately through C3, C6, C9 and C12. As a result, the side of the host that contains the guest methyl groups is more “open” to the outside, and the other side is more “closed”. Second, the N atoms are about 0.2 Å away from the $\text{Cu}\cdots\text{Cu}'$ vector, in the direction of the guest CH_3 group; this displacement results in less repulsion between the $\text{Cu}_2(\text{NBA})_2$ and 2-Mepyz moieties than would be present if the $\text{Cu-N}\cdots\text{N-Cu}$ linkage were completely linear.

We propose that the rotation of the two $(\text{acac})_2$ planes, and the displacement of the guest molecule away from the $\text{Cu}\cdots\text{Cu}'$ vector, result from the steric effects of the guest methyl group. They may also represent the kinds of distortion in the host and in the host-guest interaction that are important in guest release and exchange processes. The separation between mirror-related O atoms is smaller on the “closed” side of the complex (average of $\text{O2}\cdots\text{O2}'$ and $\text{O3}\cdots\text{O3}'$, 7.61 Å; see Table 2) than on the “open” side (average of $\text{O1}\cdots\text{O1}'$ and $\text{O4}\cdots\text{O4}'$, 7.91 Å); the latter value is similar to that observed for O atoms on both sides in $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2,5-Me}_2\text{pyz)})\cdot 4\text{CH}_2\text{Cl}_2$ (7.85–7.91 Å [8]). Likewise, the $\text{Cu}\cdots\text{Cu}$ distance in the 2-Mepyz adduct, 7.48 Å, is significantly smaller than that in the 2,5-Me₂pyz adduct (average 7.58 Å [8]). These structural changes are consistent with the trend in binding constants for $\text{Cu}_2(\text{NBA})_2$ in CHCl_3 solution: pyrazine, 5 M^{-1} [7]; 2-Mepyz, 2.8 M^{-1} ; and 2,5-Me₂pyz, 0.83 M^{-1} [8].

The least-squares plane formed by Cu, Cu', C6, C6', C12 and C12' (labeled P1 in Figure 1a) is a useful reference point. This plane makes the following angles with other planes in the structure: the naphthalene planes C13-C18 (along with the mirror-related atoms C13', C14', C15' and C18'; labeled P2) and C19-C24 (and C19', C20', C21' and C24'; labeled P3), $33.35(7)^\circ$ and $4.06(7)^\circ$ respectively; and the pyz moiety N1P, C3P, C4P, N2P, C5P and C6P (labeled P4), $84.4(2)^\circ$.

Another measure of the orientation of the 2-Mepyz guest molecule is the O1-Cu-N1P-C6P torsion angle, $-53.8(6)^\circ$. The analogous torsion angles in $\text{Cu}_2(\text{NBA})_2(\mu\text{-(2,5-Me}_2\text{pyz)})\cdot 4\text{CH}_2\text{Cl}_2$ are $-51.2(5)$ and $-50.4(5)^\circ$ [8]. Thus, the conformations of the 2-Mepyz and 2,5-Me₂pyz guests are within a few degrees of one another.

Short intermolecular contacts in the present structure are of two types: within the layers of molecules perpendicular to b ; and between adjacent layers. Molecules within the layers are arranged in a herringbone pattern with the naphthalenediyl moiety of one host contacting the host and guest of the next complex (see top view in Figure 3). The close approach of adjacent layers (see discussion below), which are approximately 3.5 Å apart, involves four C1S-H \cdots O interactions linking O2 and O3 of one host with O1 and O4 of a host (at $\frac{1}{2} - x, -y, \frac{1}{2} + z$) in the next layer: H1S1 \cdots O2, 2.46 Å; H1S1 \cdots O3, 2.42 Å; H1S2 \cdots O1, 2.54 Å; and H1S2 \cdots O4, 2.41 Å.

Structure of $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$

This structure (see Figure 2) consists of centrosymmetric binuclear Cu complexes with two *exo*-bound CH_3CN molecules, and disordered solvent molecules in general positions. The general framework of the molecule is very similar to that of $\text{Cu}_2(\text{XBA})_2$ [6]. The *m*-xylylene and $\text{Cu}(\text{acac})_2$ least-squares planes are nearly perpendicular (dihedral angle $87.86(5)^\circ$).

The $\text{Cu}\cdots\text{Cu}'$ distances in $\text{Cu}_2(\text{XBA})_2$ (4.901(3) Å) [6] and $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ (4.8302(12) Å) are similar. The Cu atoms in the CH_3CN adduct are pulled away from the center of the molecule by the axial ligands (0.1526(9) Å out of the plane of the coordinated O atoms). In order to accommodate this pyramidal environment about Cu while leaving the $\text{Cu}\cdots\text{Cu}'$ distance slightly shorter than that in $\text{Cu}_2(\text{XBA})_2$, other parts of the $\text{Cu}(\text{acac})_2$ moieties are significantly closer together than in $\text{Cu}_2(\text{XBA})_2$ [6]. For example, the closest intramolecular O \cdots O distances across the $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2$ molecule are O1 \cdots O3' (4.503(3) Å) and O2 \cdots O4' (4.547(2) Å); analogous distances in $\text{Cu}_2(\text{XBA})_2$ [6] are 4.858(7) and 4.927(7) Å.

The electron density in the solvent region in $\text{Cu}_2(\text{XBA})_2(\text{CH}_3\text{CN})_2\cdot 1.5\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ was modeled as follows. The CH_3CN molecule C1S-C2S-N1S is in a general position. Additional electron density in this region was modeled by a water molecule (O6; O6 \cdots C1S 0.543(8) Å), with 25% occupancy, and the occupancy of C1S-C2S-N1S was set to 75%. The remaining partially occupied water molecule (O5) is also in a general position, but close to the inversion center at 0, 0.5, 0 (O5 \cdots O5' 2.422(10) Å). The closest intermolecular contacts are between the CH_3 group of a coordinated acetonitrile molecule and the adjacent $\text{Cu}_2(\text{XBA})_2$ moiety: C20 \cdots O1 3.333(3), C20 \cdots O2 3.317(3) and C20 \cdots O4 3.176(3) Å.

The apparent presence of water in these crystals is consistent with our observations concerning their formation. Crystallization experiments with $\text{Cu}_2(\text{XBA})_2$ in $\text{CHCl}_3\text{-CH}_3\text{CN}$ mixtures generally yield primarily or exclusively olive-green needles of anisotropic $\text{Cu}_2(\text{XBA})_2$ at first (i.e. 1–

Table 4. Coordination environments in Cu(β -diketonato)₂L and related species

Molecule	Cu...Cu ^a	Cu-N ^b	Cu...-(O, O, O, O) ^c	Ref.
Cu ₂ (NBA) ₂ (μ -(2-Mepyz))	7.4801(8)	2.341(11), 2.376(11)	0.142(1)	d
Cu ₂ (NBA) ₂ (μ -(2,5-Me ₂ pyz))	7.596(2), 7.559(2)	2.452(7), 2.374(7)	0.141(2), 0.155(2)	8
Cu ₂ (NBA) ₂ (μ -Dabco)	7.401(4)	2.42(1)	0.175(2)	7
Cu ₂ (XBA) ₂ (CH ₃ CN) ₂	4.8302(12)	2.368(2)	0.1526(9)	d
[Cu(hfac) ₂] ₂ (μ -pyz)	7.287	2.25(2)	0.24(1)	14
[Cu(hfac) ₂] ₂ (μ -Dabco)	7.097, 7.127	2.23(1), 2.27(1), 2.262(7)	0.240(4), 0.271(4), 0.251(4)	15
(4-picoline)Cu(hap) ₂ ^e	–	2.27(2)	0.27(2)	16
Cu(acac) ₂ (quinoline)	–	2.36(1)	0.186(3)	17

^a Distance/Å between Cu atoms in binuclear complexes.

^b Apical Cu-N distance/Å.

^c Distance/Å from Cu to least-squares plane of four equatorial O atoms.

^d This work.

^e hapH = 2'-hydroxyacetophenone.

Table 5. Unit-cell parameters for M₂(NBA)₂(μ -G) complexes

M	G	Space grp	Z	a/Å	b/Å	c/Å	β /°	Ref.
Cu	2-Mepyz	<i>Pnma</i>	4	22.4674(11)	22.230(2)	11.4520(6)	90	^a
Cu	2-Mepyz	<i>Pnma</i>	4	22.786(3)	22.382(5)	11.572(6)	90	^b
Cu	Dabco	<i>Pnma</i>	4	22.771(6)	22.326(5)	11.621(3)	90	7
Cu	2,5-Me ₂ pyz	<i>C2/m</i>	4	22.941(6)	22.432(4)	11.677(2)	97.32(2)	8
Zn	Dabco	<i>C2/m</i>	4	22.650(2)	22.270(2)	11.707(2)	97.11(2)	18
Cu	piperazine	<i>P1</i>	2	10.5929(6)	11.4581(8)	14.1552(10)	104.32(1) ^c	18
Zn	piperazine	<i>Pbca</i>	4	24.085(2)	22.176(2)	9.670(2)	90	18

^a This work; measured at 100 K.

^b This work; measured at 298 K.

^c Triclinic; $\alpha = 90.26(1)^\circ$; $\gamma = 94.25(1)^\circ$.

2 days). However, after standing for several additional days, turquoise crystals of the CH₃CN adduct begin to form. This is expected if the presence of water is *required* for crystallization: the solutions are likely to absorb water from moist laboratory air over a period of days.

Square pyramidal coordination environments

Nearly all copper(II) β -diketone complexes are square planar, and the coordination of a fifth ligand usually leads to a square pyramidal adduct. This type of square-pyramidal geometry is found in both of the structures described here. Despite the gross structural differences between Cu₂(NBA)₂(μ -(2-Mepyz)) and Cu₂(XBA)₂(CH₃CN)₂, the Cu coordination environments in the two structures (as indicated by the Cu-N distances and the deviations of the Cu atoms toward N and away from the β -diketone O atoms) are very similar. These quantities are compared with those for a variety of related structures, including [Cu(hfac)₂]₂(μ -pyz) [14], [Cu(hfac)₂]₂(μ -Dabco) [15], (4-picoline)Cu(hap)₂ (hapH = 2'-hydroxyacetophenone) [16] and Cu(acac)₂(quinoline) [17], in Table 4. The Cu-N distances are shortest in the adducts of Cu(hfac)₂; this is as expected because the strongly electron-withdrawing hfac⁻ ligands make Cu(hfac)₂ a strong Lewis acid.

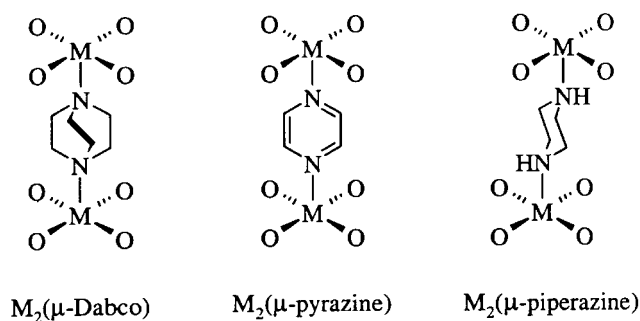
The pyramidal character of the Cu coordination environment (i.e. the deviation of the Cu atoms from the O atom least-squares plane) is also typical for the present structures: except for the hfac complexes, none of the other structures shows a deviation greater than 0.19 Å. Among the three Cu₂(NBA)₂(μ -G) structures studied thus far, that with G = Dabco shows the greatest deviation. This is reasonable, since the “size” of Dabco, as measured by its intramolecular N...N distance, is ca. 0.2 Å smaller than that of pyrazine; thus, in order to keep the Cu-N distances roughly constant, the Dabco guest should cause a greater pyramidal distortion than the pyrazines. We had hoped that the Cu₂(XBA)₂(CH₃CN)₂·1.5CH₃CN·H₂O structure, with its *exo*-coordinated apical ligands, would provide an example of a less strained Cu coordination environment for comparison with the Cu₂(NBA)₂(μ -G) structures. However, we find no clear pattern for the set of unbridged structures, and Cu₂(XBA)₂(CH₃CN)₂·1.5CH₃CN·H₂O, to distinguish them from the *endo* systems. The square-pyramidal coordination environment about Cu is very similar in the two structures, despite the fact that Cu₂(NBA)₂(μ -(2-Mepyz)) is internally strained; this suggests that the apical Cu-N interaction is relatively rigid. In other words, changes in guest size and shape are accommodated by the Cu₂(NBA)₂ host primarily through slight changes in the geometry of the organic

framework, rather than changes in coordination geometry at Cu.

Crystal packing in $M_2(NBA)_2(\mu-G)$ complexes

The intermolecular contacts in $Cu_2(NBA)_2(\mu-(2-MepyZ))$, within and between layers of molecules perpendicular to b , have been discussed in Section 3.1 above. We have observed similar crystal packing in several other $M_2(NBA)_2(\mu-G)$ structures. Unit-cell parameters for the other structures are summarized in Table 5. For three of the Cu structures and for $Zn_2(NBA)_2(\mu-Dabco)$ [18], the lengths of the cell axes are very similar. Also, although these four compounds crystallize in two different space groups, $Pnma$ and $C2/m$, the molecules pack in layers perpendicular to b in both structure types. The packing for $Cu_2(NBA)_2(\mu-(2-MepyZ)) \cdot 4CH_2Cl_2$ is illustrated in Figure 3. Adjacent molecules are arranged in "strips" with a diagonal orientation along the c axis, with the diagonals reversed from one "strip" of molecules to the next (in both the b and a directions). In the monoclinic structures ($C2/m$), the two orientations of molecules are the two crystallographically independent molecules in the asymmetric unit, whereas in the orthorhombic structures ($Pnma$) the different orientations are produced by screw axes or glide planes. This similarity of packing suggests that the character of the guest molecules (for pyrazines and Dabco) and the metal atoms (Cu or Zn) has little effect on intermolecular attractive forces.

The last two entries in Table 5, the $Cu_2(NBA)_2$ and $Zn_2(NBA)_2$ adducts with piperazine [18], clearly differ from the other four. This may be because the piperazine guest molecule, unlike the pyrazine derivatives and Dabco previously studied, is likely to lead to a nonlinear $M-N \cdots N-M$ linkage. The diagram below compares the $M_2(\mu-G)$ moieties with three guests. In Dabco and pyrazine, the N lone pairs lie directly along the $N \cdots N$ axis; thus, the $M-N \cdots N-M$ group is expected to be linear. In piperazine, however, equatorial substituents at the N atoms are not collinear; as a result, one $M(acac)_2$ moiety in a $M_2(NBA)_2(\mu-piperazine)$ complex is expected to be shifted horizontally with respect to the other. The resulting change in the shape of the $M_2(NBA)_2(\mu-piperazine)$ molecules may be sufficient to interfere with packing them in layers like those observed in the Dabco and pyrazine adduct structures.



Conclusions

The cofacial bis(β -diketone) complexes $Cu_2(XBA)_2$ and $Cu_2(NBA)_2$ provide cavities of well-defined size and shape. A variety of molecules bind in the *endo* or *exo* fashion to the complexes, depending on the number of donor atoms available and the match between the added molecule and the cavity size in the bis(β -diketone) complex. Experiments now in progress involve the adaptation of these host-guest reactions to complexes with functionalized bridging ligands, so that chemical transformations can be performed on the bound guest molecules.

Acknowledgements

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Improvements to the LSU X-ray Crystallography Facility were supported by the Louisiana Board of Regents, through Grants LEQSF(1996-97)-ENH-TR-10 and LEQSF(1999-2000)-ENH-TR-13.

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